JOC The Journal of Organic Chemistry
Article
pubs.acs.org/joc

Method for the Preparation of Derivatives of Heptiptycene: Toward Dual-Cavity Baskets

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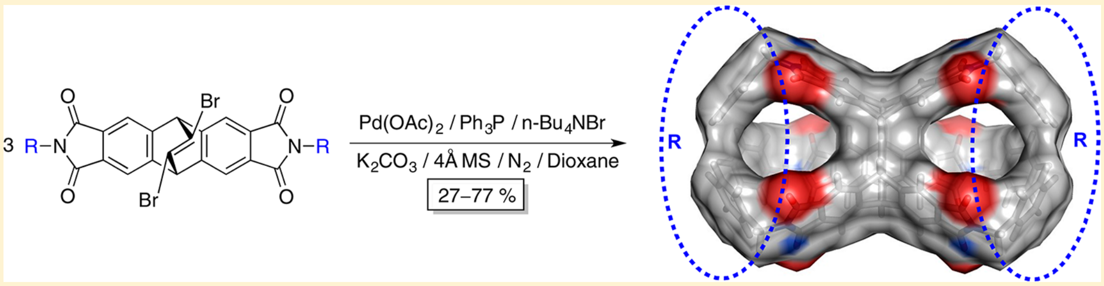
Supporting Information



ABSTRACT: We have developed a novel synthetic method that enables the preparation of functional derivatives of heptiptycene, i.e., cavitands with two juxtaposed cavities. The homocoupling of bicyclic dibromoalkenes is promoted by $Pd(OAc)_2$ (10%) in dioxane (100 °C) to give cyclotrimers in 27−77% yield under optimized reaction conditions (Ph_3P, K_2CO_3, n-Bu_4NBr, N_2, 4 Å MS). These dual-cavity baskets show a strong $\pi \rightarrow \pi^*$ absorption at 241 nm (ε = 939 000 M^{-1} cm^{-1}), along with a subsequent fluorescence emission at 305 nm.

INTRODUCTION

About four decades ago, Huebner and co-workers reported on the preparation and solid-state structure of heptiptycene (**1**) (Figure 1).[1] This D_{3h}-symmetric cavitand is formally a derivative of triptycene[2] with two enforced cavities sharing a benzene "floor". The host−guest characteristics of heptiptycene have not been studied, although this open-cavity hydrocarbon might exhibit modest (if any) affinity[3,4] toward the entrapment of properly sized/shaped guests.[5] We reason that encircling the space[6] in **1** (Figure 1) shall permit for trapping useful analytes,[7] promoting supramolecular catalysis[8,9] or studying gated molecular encapsulation.[10−13] A synthetic method for obtaining functional derivatives of **1** (Figure 1) is, however, not available, thereby preventing the corresponding recognition/reactivity studies. Indeed, a series of fascinating double-cavity cages with intriguing photophysical characteristics were built from truxene derivatives.[14] Due to their optical properties,[15] these compounds could be used as chemosensors or for building organic electronic devices.[16]

RESULTS AND DISCUSSION

In the original synthesis of heptiptycene (**1**), the cyclotrimerization of 11-chloro-9,10-dihydro-9,10-ethenoanthracene (**4**) (Figure 1) was promoted by n-BuLi to give this compound in approximately 20% yield.[2] In fact, Hart and co-workers showed[17] that strong base (BuLi) abstracts the vinylic proton in **4** to give carbanion **5** that is persistent at low temperatures (−78 °C). At high temperatures (>25 °C), however, this carbanion eliminates LiCl to give rise to the transient bicycloalkyne intermediate **6** (Figure 1). In a series of somewhat related experiments, Gassman and co-workers presented compelling evidence for the existence of norbornyne intermediates.[18] Furthermore, as shown in Figure 1, compound **6** reacts with **5** to give nucleophilic compound **7**, which subsequently traps another bicycloalkyne **6**. Finally, trimer **8** undergoes a thermal electrocyclic (6π) ring-closure followed by LiCl elimination to give heptiptycene (**1**). Alternatively, Komatsu and co-workers have shown[4] that the lithiation of 2,3-dibromobicyclo[2.2.2]oct-2-ene could give a trimeric dibromoalkene, which yields the desired cyclotrimer after a reductive cyclization. The yield of lithium-based cyclotrimerizations could indeed be improved with the addition of Cu(I) salts,[19,20] although the necessity of using a strong base as well as the occurrence of nucleophilic intermediates limit the scope of this methodology! In other words, with the carbanion-mediated approach, one could prepare a narrow range of heptiptycenes in a relatively low yield.

To address the quandary about the annulation of bicyclic cyclotrimers,[21] De Lucchi and co-workers[22] as well as others[23−26] have shown that the cyclotrimerization of bicyclic vinyl halides can be promoted with Cu(I),[27,28] Cu(II),[29] or Pd(0)[30,31] transition-metal complexes. In these procedures, mild reaction conditions enabled the preparation of a variety of

Received: December 26, 2012
Published: February 27, 2013

dx.doi.org/10.1021/jo3027998 | J. Org. Chem. 2013, 78, 2984−2991

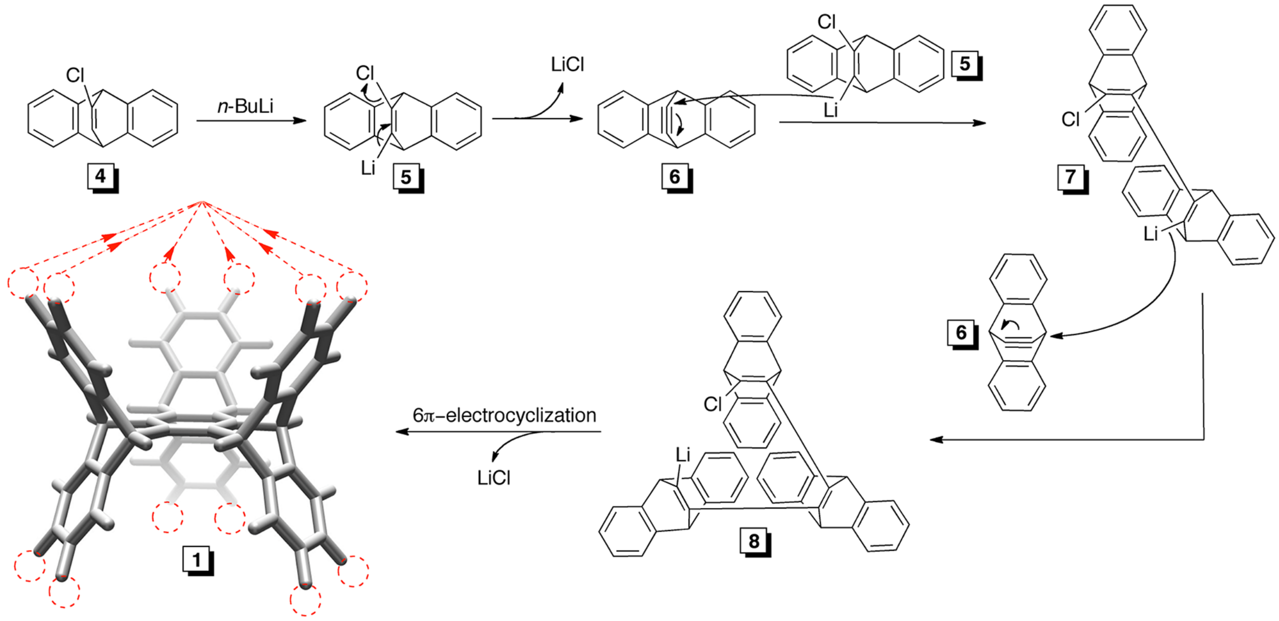
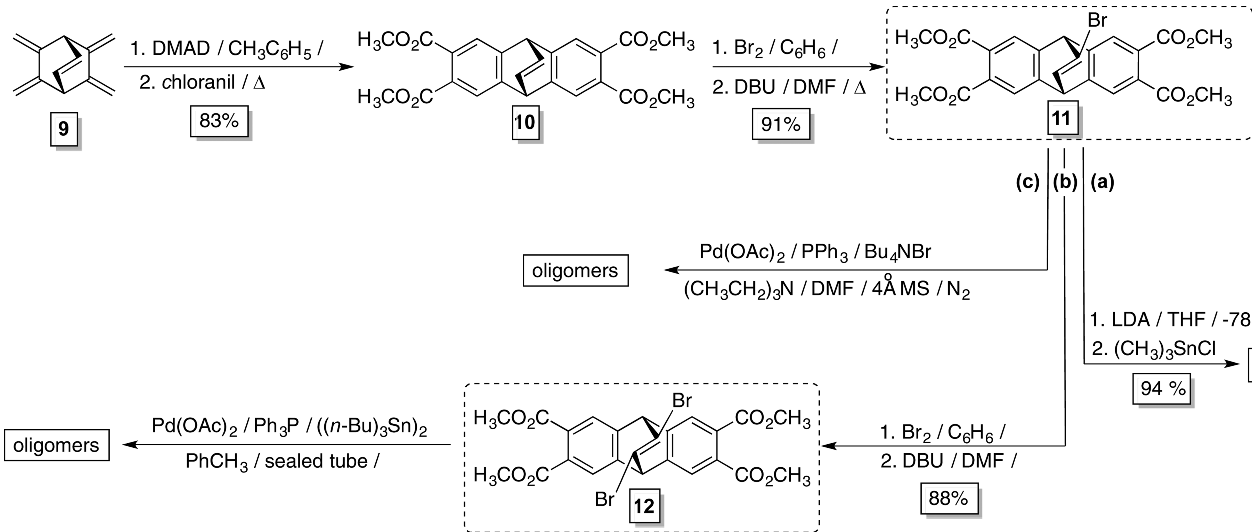


Figure 1. Original synthesis of heptiptycene **1** started with compound **4**.[1] The formation of reactive intermediates **5−8** was validated with a series of trapping experiments.[17]

Scheme 1. Synthesis of Compounds 11 and 12 and Their Reaction with $Pd(OAc)_2$ under the (b) Heck[31] and (c) Griggs[30] Coupling Conditions



cyclotrimers in good to excellent yields.[22] In line with such important findings, we reasoned that the synthesis of functionalized heptiptycenes could be accomplished following literature protocols[22] and set to examine the hypothesis.

In order to create bicyclic vinyl halides of types **11** and **12** (Scheme 1) and subsequently examine their cyclotrimerization,[22] we attempted the cycloaddition of bis(trimethylsilyl)-acetylene (BTMSA) to tetramethyl anthracene-2,3,6,7-tetracarboxylate (at reflux in CH_3OH/H_2O = 1:1). Interestingly, the reaction gave no desired cycloadduct in spite of the matching electronic characteristics of the reactants.[32] In another synthetic route, we began with tetramethylidene compound **9** (Scheme 1), which could be prepared in gram quantities following published procedures.[33] In the Diels−Alder reaction of dimethyl acetylenedicarboxylate (DMAD) and **9**, followed by oxidation of the cycloadduct with chloranil (tetrachloro-*p*-benzoquinone), we obtained tetraester **10** in an overall 83% yield. This compound was efficiently brominated,[34] using a low concentration of Br_2 (presumably, via radical addition[35]), to give the vicinal dibromo product; moreover, such reaction conditions were necessary to circumvent Wagner−Meerwein rearrangements occurring with the ionic addition of Br_2 to bicyclic compounds of type **10**.[36,37] After dehydrobromination (DBU), we obtained the bromo-olefin **11** and subsequently attempted stannylation under standard reaction conditions (pathway a, Scheme 1);[38] note that bromostannylated alkenes are known to undergo cyclotrimerization reactions.[22] Interestingly, the reduction of **11** into **10** took place with no formation of the desired compound (Scheme 1). To avoid complications encountered in the stannylation, we investigated the cyclotrimerization of dibromoalkene **12** by following the methodology developed by Grigg (pathway b, Scheme 1).[30] Under

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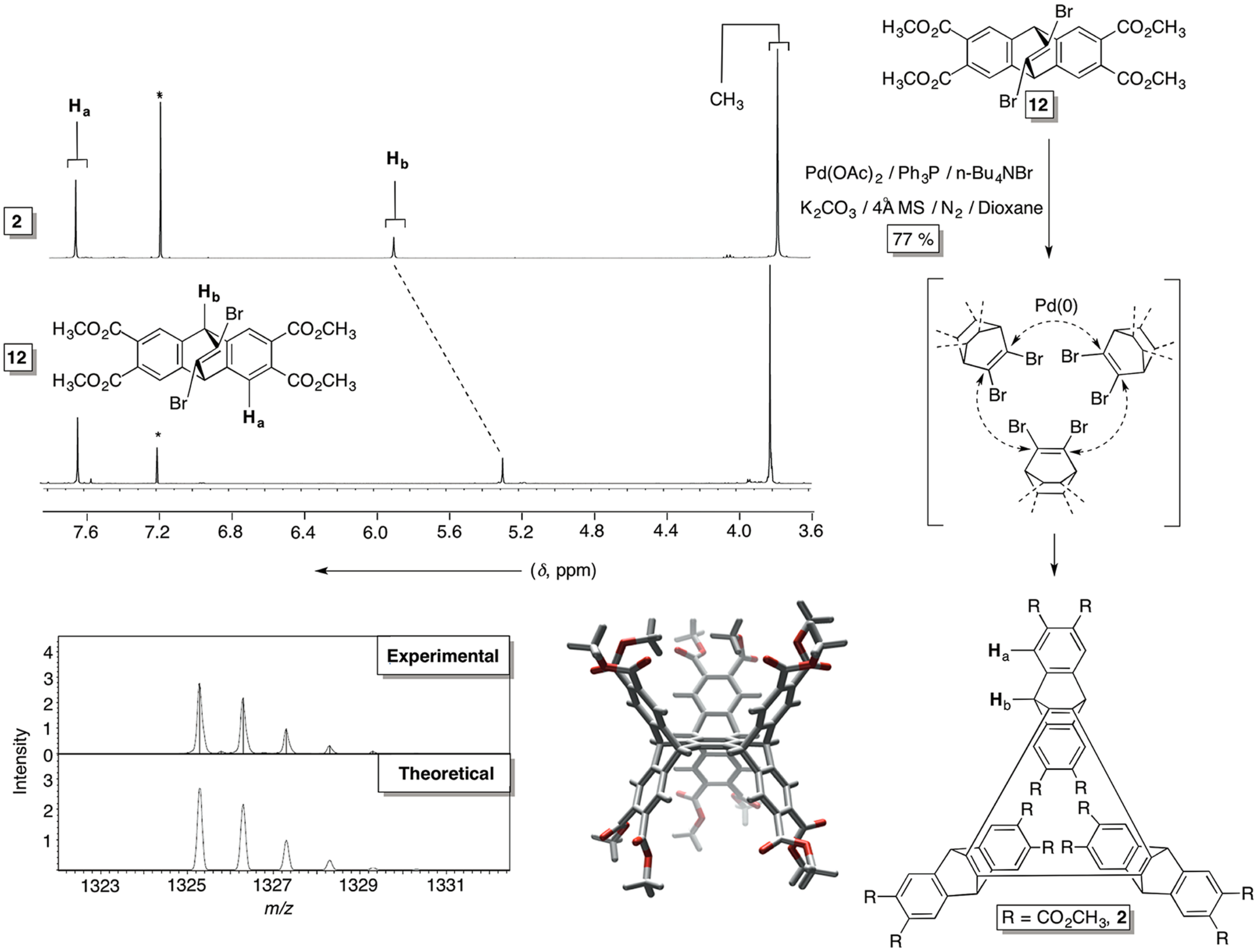

Figure 2. (Top) ^{1}H NMR spectra (500 MHz, $CDCl_3$) of compounds **12** and **2** at 298.0 K. (Right) Homocoupling of **12** is promoted by $Pd(OAc)_2$ to give dodecamethyl ester heptiptycene (**2**); energy-minimized structure of compound **2** (Spartan, MMFFs) is shown on the right. (Bottom) Principal signal in ESI-MS spectra of **2** corresponds to the $[M + Na]^+$ cation, with consistent theoretical and experimental distributions of isotopes.

these conditions, we observed the oligomerization process (^{1}H NMR spectroscopy) and at both higher (30−100 mM) and lower (10 mM) concentrations of dibromoalkene reactant **12** (pathway b, Scheme 1). Subsequently, we decided to probe the cyclotrimerization of **11** using optimized Heck-type[39] conditions (pathway c, Scheme 1). In this case, the conversion of **11** (10−30 mM)[31] into oligomers (^{1}H NMR spectroscopy) appeared as the principal reaction pathway (Scheme 1); in this case, we also observed (^{1}H NMR spectroscopy) the formation of only trace quantities of the desired cyclized **2**.

Since the Heck-type coupling of bromoalkene **11** failed to give the desired cyclotrimer **2**, we were intrigued to discover if dibromoalkene **12** could form **2** under similar experimental conditions (Figure 2). In fact, Dyker reported[40] that aryl diiodides dissolved in DMF and in the presence of $Pd(OAc)_2$/K_2CO_3/*n*-Bu_4NBr undergo palladium-catalyzed annulation to give Ullmann-type products. The homocoupling of vinyl halides is, however, less common,[41] but nonetheless known,[42,43] to produce dienes in satisfactory yields. *Markedly, compound* **12** *cyclotrimerized into the desired* **2** *(77% yield, Table 1) when promoted by* $Pd(OAc)_2$ *(10%) in dioxane and in the presence of* K_2CO_3/Ph_3P/*n*-Bu_4NBr/*4 Å molecular sieves*! The ^{1}H NMR spectrum of D_{3h}-symmetric **2** (Figure 2) has three signals and is akin to the one corresponding to monomeric **12**. In particular,

Table 1. Varying the Concentration of 12 Affects the Outcome of Its Cyclotrimerization with $Pd(OAc)_2$ (10 mol %) in Anhydrous Dioxane at 100 °C^a

entry	solvent	conc of **12** (mM)	product **2** (% yield)
1	dioxane	5	21
2	dioxane	10	77
3	dioxane	15	36
4	dioxane	30	6
5	DMF	5	oligomers
6	acetonitrile	5	no reaction

^{a}In each reaction, we used Ph_3P (20 mol %), K_2CO_3 (10 molar equiv), *n*-Bu_4NBr (2.0 molar equiv), and pulverized 4 Å molecular sieves.

^{1}H NMR resonance of the bridgehead H_b proton in **2** is shifted further downfield ($\Delta\delta$ = 0.7 ppm, Figure 2) via, presumably, magnetic deshielding of this proton by the central benzene ring (Figure 2). Furthermore, the isotope distribution of the sodiated parent ion $[M + Na]^+$ in the electrospray ionization mass spectrum of **2** concurs with the atomic composition of this molecule (Figure 2). Interestingly, varying the concentration of dibromoalkene **2** altered the course of the cyclotrimerization:[44] at lower (<10 mM) or higher (>15 mM) concentration of the reactant, the yield would drop

dx.doi.org/10.1021/jo3027998 | J. Org. Chem. 2013, 78, 2984−2991

considerably (Table 1); the reaction was experimentally examined with up to ~100 mg of the starting material. The nature of the solvent appears to have an effect on the catalytic cycle[45] with more polar acetonitrile/DMF inhibiting the formation of dual-cavity **2** (Table 1). Finally, the Ph_3P, K_2CO_3, and n-Bu_4NBr reagents were all necessary for an effective homocoupling of **12** (Table 2): by altering or completely removing one reactant at the time, the reaction's outcome changed giving rise to oligomers and/or undesired products (Table 2).[40,41,43,46] What is the mechanism for the catalytic conversion of **12** into dual-cavity **2**? On the basis of earlier studies,[40,41,47] we presume that the observed homocoupling encompasses a disproportionation of two R−Pd(II)−Br species (generated in the oxidative addition) into Pd(0), homocoupled product R−R and $PdBr_2$; the ligand exchange (transmetalation) is postulated to occur via σ-bond metathesis, comprising a four-center transition state. The reduction of Pd(II) into Pd(0) is perhaps promoted with tributylamine,[40,48,49] formed in situ via decomposition of the quaternary salt[50] at high temperature by the formally reversed Menshutkin reaction.[51] Triphenylphosphine, in combination with potassium carbonate, was previously shown to act as a reductant[43] of the palladium(II) cation, although an excess of Ph_3P (>1 molar equiv) was found to inhibit the transformation (Table 2).

Table 2. Cyclotrimerization of 12 (10 mM) Examined in Anhydrous Dioxane at 100 °C with $Pd(OAc)_2$ (10 mol %)[a]

entry	ligand	base	molecular sieves	quaternary salt	product (% yield)
1	PPh_3	Et_3N	+	n-Bu_4NBr	oligomers
2	PPh_3	Pyridine	+	n-Bu_4NBr	oligomers
3	PPh_3	K_2CO_3	+	n-Bu_4NBr	**2** (77)
4	*c*	K_2CO_3	+	n-Bu_4NBr	**10** (95)
5	PPh_3	K_2CO_3	+	n-Me_4NBr	**10** (95)
6	PPh_3	K_2CO_3	+		no reaction[b]
7	PPh_3	K_2CO_3	−	n-Bu_4NBr	no reaction[b]

[a]In each reaction, we used ligand (20 mol %), base (10 mol equiv), quaternary ammonium salt (2 mol equiv), and pulverized 4 Å molecular sieves. [b]Trace amount of product **2** was observed with ^1H NMR spectroscopy. [c]An excess of Ph_3P (>1 mol equiv) inhibits the reaction.

A functionalization of 12 esters in heptiptycene **2** (Figure 2) would give an intriguing multivalent receptor comprising two juxtaposed cavities (Figure 3). Importantly, each of the 12 reactions must, in a linear synthesis, be high yielding to give useful quantities of the product.[52,53] Alternatively, we set to probe a convergent strategy for obtaining dual-cavity baskets of type $\mathbf{3_{a\text{-}c}}$ (Figure 3). First, we converted compound **12** into bisimides $\mathbf{13_{a-c}}$ carrying the desired functional groups at the periphery. Then, we completed the homocoupling of the dibromoalkenes with $Pd(OAc)_2$ to obtain $\mathbf{3_{a-c}}$ in 27−47% yield. Evidently, the cyclotrimerization procedure could be used for obtaining various derivatives of heptiptycene: one can place aliphatic (R = $CH_2CH_2CH_3$, $\mathbf{3_a}$), benzylic (R = $CH_2C_6H_5$, $\mathbf{3_b}$) or aromatic (R = C_6H_5, $\mathbf{3_c}$) groups at the rim of the fused southern and northern cavitands (Figure 3).

With proper functional groups at the rim of the dual-cavity baskets (Figure 3), one could turn these multivalent compounds into chemosensors or catalysts.[54−57] Accordingly, understanding the absorption as well as emission characteristics of dual cavitands is important for assessing a potential application in the area of sensor design.[58−60]

Compounds **14**, **15**,[61] and $\mathbf{3_b}$ comprise an increasing number of phthalimide chromophores (from one to six, Figure 4),

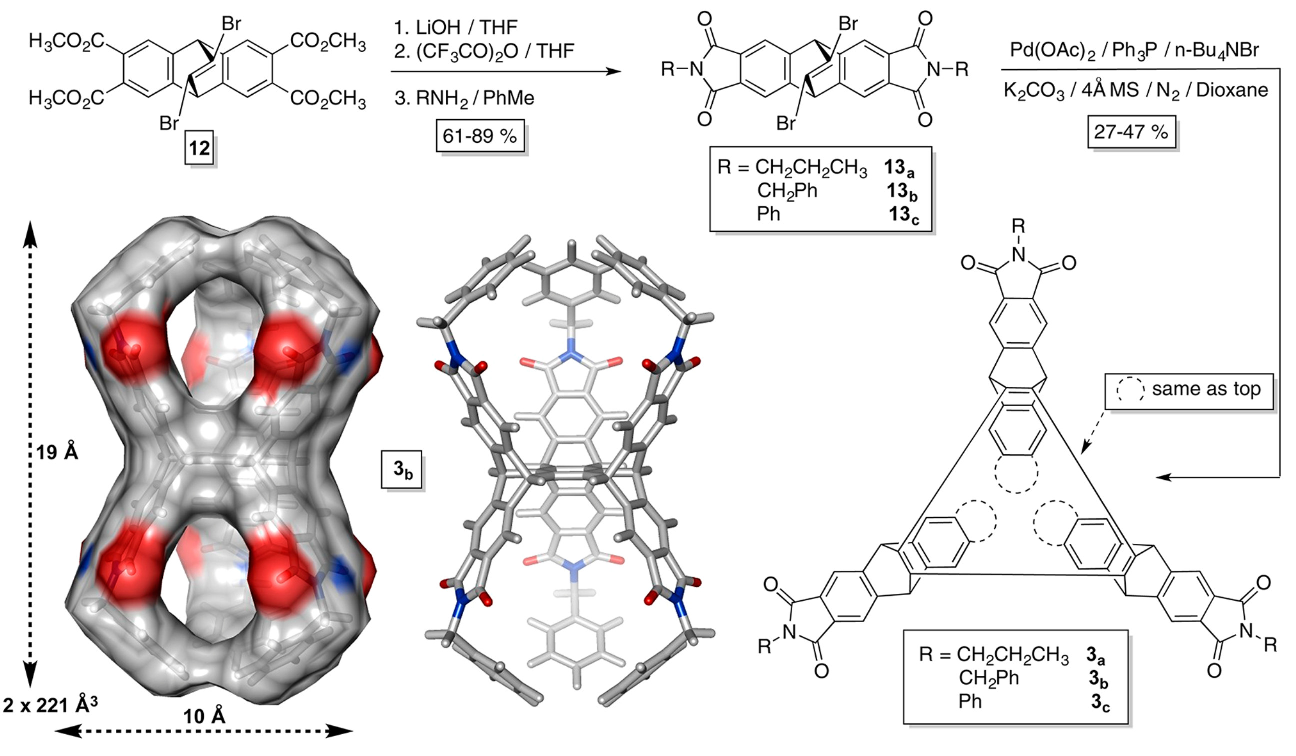

Figure 3. (Top) Synthesis of dual-cavity baskets $\mathbf{3_{a-c}}$. (Bottom) Energy-minimized structure of $\mathbf{3_b}$ (MMFFs) and van der Waals surface of this cavitand.

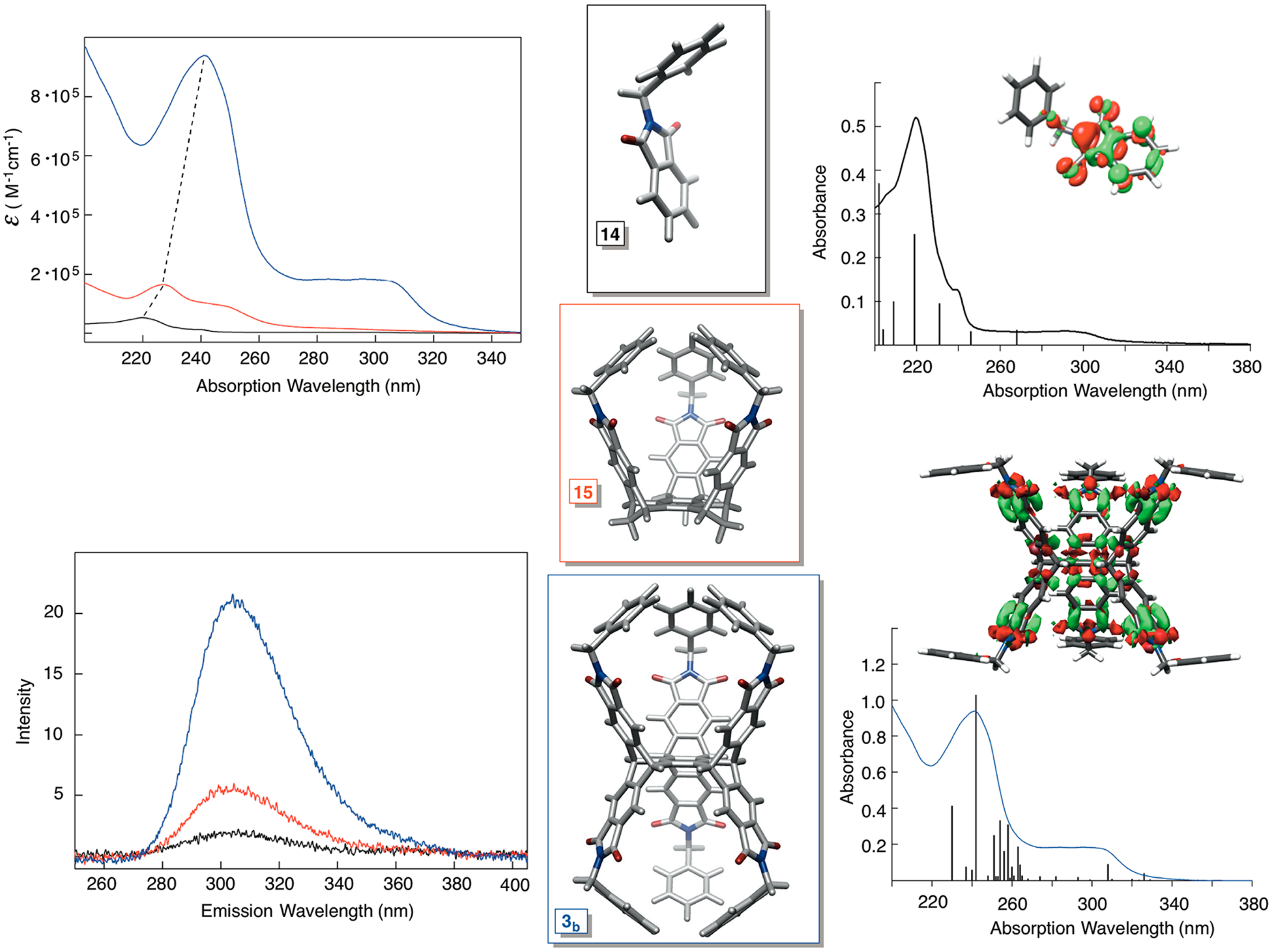

Figure 4. UV−vis and emission spectra (λ_{ex} = 220 nm, CH_3CN) of compounds **14** (black box), **15** (red box), and $\mathbf{3_b}$ (blue box) were obtained at 298 K; for the emission measurements, each sample was 0.1 μM. Computed (B3LYP/SV(P)) electronic transitions of **14** (top right) and $\mathbf{3_b}$ (bottom right) along with difference density plots corresponding to transitions at 219 and 242 nm, respectively; note that the red contours represent the depletion of electron density from the ground state, while the green contours represent the accumulation of electron density in the excited state.

which in two baskets are embedded within their bicyclic framework. The UV−vis spectrum of the model compound **14** showed an electronic transition at 220 nm (ε = 56000 M^{-1} cm^{-1}, Figure 4) that is presumed to be of $\pi \rightarrow \pi^*$ character[62−65] in addition to a less prominent band at 237 nm (ε = 12800 M^{-1} cm^{-1}, Figure 4). Interestingly, the $\pi \rightarrow \pi^*$ transition at 220 nm becomes red-shifted in C_3-symmetric basket **15** ($\Delta\lambda$ = 7.0 nm, Figure 4) and even more red-shifted in D_{3h}-symmetric $\mathbf{3_b}$ ($\Delta\lambda$ = 21.0 nm, Figure 4); thus, there ought to be a conjugative interaction between the chromophores, despite their formal "isolation" with saturated carbon atoms.[66] Moreover, the intensities of the $\pi \rightarrow \pi^*$ transitions at λ_{max} ($\varepsilon_{15}{\rightarrow}\varepsilon_{16}{:}\varepsilon_{3b}$ = 1:3.2:18, Figure 4) increases with the number of phthalimide units (1:3:6, Figure 4): the proportion of the extinction coefficients exceeds the number of phthalimides.

To obtain more insight into the photophysical characteristics of these compounds, we computed the electronic spectra of **14** and **3b** using time-dependent[67] density functional theory (B3LYP/SV(P)).[68−70] In particular, model compound **14** was found to exhibit an electronic transition of $\pi \rightarrow \pi^*$ character at 219 nm,[62,63] consistent with the experimental data (Figure 4). Furthermore, the computed UV−vis spectrum of **3b** shows a pronounced vertical excitation at 242 nm (Figure 4), corroborating the observed red shift of the $\pi \rightarrow \pi^*$ transition. In fact, the electron density difference plot[71] of **3b** (Figure 4) indicates a delocalization of the electron density of the corresponding transition contributing to the observed $\pi \rightarrow \pi^*$ shift (Figure 4). *N*-Alkylphthalimides exhibit a rather weak emission characterized with a low quantum yield ($\Phi \sim 10^{-3}$).[72] Upon excitation at 220 nm, the emission intensity from dual-cavity basket $\mathbf{3_b}$ appeared 4 times greater than in **15** and 12 times greater than in model compound **14** (Figure 4). Apparently, embedding a phthalimide chromophore within a rigid bicyclic framework of dual-cavity **3** improves the efficiency of the fluorescence emission, which could potentially be used for signaling the presence of various analytes.

■ CONCLUSION

In conclusion, palladium acetate promotes the homocoupling of dibromoalkenes into a variety of functional heptiptycenes.[6] The cyclotrimerization procedure complements those already available in the literature[22] and will be of interest for the preparation of multivalent dual-cavity hosts that could, perhaps, report on the presence of small guest molecules in organic and aqueous media[73] or promote chemical reactions inside the confined environments.[74]

■ EXPERIMENTAL SECTION

General Methods. All chemicals were purchased from commercial sources and were used as received, unless stated otherwise. All solvents were dried prior to use according to standard literature protocols. Chromatography purifications were performed using silica gel 60 (40–75 μm, 200 × 400 mesh). Thin-layer chromatography (TLC) was performed on silica-gel plates (200 μm). Chromatograms were visualized by UV light (254 nm). ^{1}H and ^{13}C NMR spectra were recorded, at 400 and 100 MHz, respectively, on a DRX-400 spectrometer. They were referenced using the solvent residual signal as an internal standard. Samples were prepared using $CDCl_3$. The chemical shift values are expressed as δ (ppm) values and the scalar coupling constants (J) are given in hertz (Hz). The following abbreviations were used for signal multiplicities: s, singlet; d, doublet; t, triplet; m, multiplet; and br, broad. High-resolution electrospray ionization mass (HRMS–ESI) spectra were recorded on a Micro-TOF ESI instrument using a CH_3OH solution of sodium formate for efficient ionization.

Compound 10. 5,6,7,8-Tetramethylenebicyclo[2.2.2]oct-2-ene (**9**) (263 mg, 1.7 mmol) was dissolved in 15 mL of anhydrous toluene and under an atmosphere of N_2 at 298 K. Freshly distilled DMAD (425 mL, 3.4 mmol) was added all at once, and the reaction mixture was heated 50 °C for 6 h. Then, *p*-chloranil (2.3 g, 9.5 mmol) was added in portions, after which the reaction mixture was brought to reflux for 24 h. After a complete oxidation of the reactant (^{1}H NMR spectroscopy), the solvent was removed under a reduced pressure. The crude product was purified by column chromatography (SiO_2, hexanes/ethyl acetate = 1:1) to yield 652 mg (83%) of **10** as a light yellow solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.60 (4H, s), 6.97 (2H, m), 5.27 (2H, m), 3.84 (12H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 168.0, 148.3, 138.6, 129.3, 123.8, 52.8, 50.8. HRMS (ESI): m/z calcd for $C_{24}H_{20}NaO_8$ 459.1056 $[M + Na]^+$, found 459.1059.

Compound 11. Compound **10** (50 mg, 0.11 mmol) was dissolved in 5.8 mL of benzene (Note: the concentration of the reactant must be kept below 0.025 M). A solution of bromine (0.13 mmol) in 1 mL of benzene was then slowly added to the reaction mixture over ∼5 min. The reaction was allowed to stir for an additional 15 min, followed by removal of the solvent under reduced pressure to yield 61 mg (0.10 mmol, 99%) of dibromoalkane **13** as a reddish-brown oil. This compound (61 mg, 0.10 mmol) was dissolved in 2 mL of anhydrous DMF followed by the addition of 1,8-diazabicycloundec-7-ene (37.4 mL, 0.25 mmol) and heating at 80 °C for 20 min. The reaction mixture was cooled to room temperature and diluted with 15 mL of ethyl acetate, and the organic layer was washed with aqueous HCl (5 × 10 mL, 5% HCl). Upon removal of the residual water (Na_2SO_4) and filtration (SiO_2), the filtrate was condensed in vacuo to give 44 mg (91%) of **11** as a white crystalline solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.707 (2H, s), 7.636 (2H, s), 7.020 (1H, dd; J = 6.4 Hz, J = 2 Hz), 5.264–5.238 (2H, m), 3.883 (6H, s) 3.879 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 167.6, 167.5, 162.7, 146.7, 146.6, 135.9, 131.4, 130.1, 129.4, 124.0, 123.7, 59.5, 52.7, 51.9. HRMS (ESI): m/z calcd for $C_{24}H_{19}BrNaO_8$ 537.0161 $[M + Na]^+$, found 537.0164.

Compound 12. This molecule was prepared in 88% overall yield following the protocol described for obtaining **11**. Note that in the bromination of **11**, the concentration of this compound ought to be kept at 0.01 M or lower in order to avoid rearrangements at room temperature. ^{1}H NMR (400 MHz, $CDCl_3$): 7.709 (4H, s), 5.364 (2H, s), 3.883 (12H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 145.4, 130.4, 129.1, 124.1, 77.5, 77.4, 77.2, 76.8, 60.3, 52.9, 52.9. HRMS (ESI): m/z calcd for $C_{24}H_{18}Br_2NaO_8$ 614.9246 $[M + Na]^+$, found 614.9239.

Compound 2. Compound **12** (25 mg, 0.054 mmol) was dissolved in 5.4 mL of anhydrous dioxane and the solution stirred under an atmosphere of nitrogen. To this, a solid "catalytic mixture" was added all at once (10 mol % of $Pd(OAc)_2$, 20 mol % of PPh_3, 2 molar equiv of n-Bu_4NBr, 10 molar equiv of K_2CO_3, and 4 Å molecular sieves in the same amount as ammonium salt) and the solution brought to reflux at 100 °C for 48 h. The reaction mixture was quenched with diluted HCl (2.5 mL) and then extracted with ethyl acetate (3 × 5 mL). The organic layer was dried over sodium sulfate, the solvent was removed in vacuum, and the crude product was purified by silica chromatography (dichloromethane/methanol = 10:1) to yield 18.0 mg (77%) of dual-cavity **2** as a white solid. ^{1}H NMR (400 MHz, $CDCl_3$): 7.739 (12H, s), 5.980 (6H, s), 3.859 (36H, s). ^{13}C NMR (400 MHz, $CDCl_3$): 167.6, 146.3, 134.9, 130.3, 124.6, 52.8, 49.5. HRMS (ESI): m/z calcd for $C_{72}H_{54}NaO_{24}$ 1325.2903 $[M + Na]^+$, found 1325.2895.

Compounds 13_{a-c}. Compound **12** (80 mg, 0.134 mmol) was dissolved in 2 mL of anhydrous THF. An aqueous solution (2 mL) of lithium hydroxide (221 mg, 5.387 mmol) was added to the reaction mixture. The reaction was kept at 80 °C for 2 h and then cooled to room temperature. The solvent was evaporated followed by the addition of aqueous HCl (5%). The solution was subsequently extracted with ethyl acetate containing 5% of methanol (5 × 30 mL), and the organic layer was evaporated to yield 66 mg (0.124 mmol, 93%) of tetraacid [(9s,10s)-11,12-dibromo-9,10-dihydro-9,10-ethenoanthracene-2,3,6,7-tetracarboxylic acid] product as a white crystalline needles. ^{1}H NMR (400 MHz, DMSO-d_6): 14.0–12.5 (4H, br), 7.827 (4H, s), 5.901 (HRMS (ESI): m/z calcd for $C_{20}H_{10}Br_2LiO_8$: 544.8882 $[M + Li]^+$, found: 544.8888. 2H, s). ^{13}C NMR (100 MHz, DMSO-d_6): 168.0, 145.2, 145.1, 129.7, 58.2. Tetraacid (66 mg, 0.124 mmol) was dissolved in 5 mL of anhydrous THF followed by the addition of 175 mL (260 mg, 1.240 mmol) of trifluoroacetic anhydride. After 30 min, the solvent was removed in vacuum to give bis-anhydride as a yellow solid in 92% yield (57 mg, 0.114 mmol). ^{1}H NMR (DMSO-d_6): 8.012 (4H, s), 6.031 (2H, s). The product was used without further purification as any characterization proved difficult due to its hydrolytic instability. To a solution of *bis*-anhydride (15 mg, 0.029 mmol) in anhydrous DMSO (0.6 mL), propylamine (3.4 mg, 0.058 mmol) was added, and the mixture was stirred for 10 min at room temperature. Pyridine (0.1 mL) was then added and the reaction temperature increased to 120 °C for 2 h. The solvent was removed in vacuum and ethyl acetate (2 mL) added, which upon sonication gave desired $\mathbf{13_a}$ as a white solid (18.3 mg, 89%). Compound $\mathbf{13_a}$. ^{1}H NMR (400 MHz, $CDCl_3$): 7.828 (4H, s), 5.544 (2H, s), 3.614 (4H, t, J = 7.2 Hz), 1.635 (4H, br.), 0.908 (6H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 167.9, 148.6, 131.4, 129.1, 118.6, 61.4, 39.9, 22.0, 11.4. HRMS (ESI): m/z calcd for $C_{26}H_{20}Br_2N_2NaO_4$ 606.9667 $[M + Na]^+$, found 606.9646. Compounds $\mathbf{13_b}$ and $\mathbf{13_c}$ were obtained (71 and 81% yield, respectively) following the preparative procedure for obtaining $\mathbf{13_a}$. Compound $\mathbf{13_b}$. ^{1}H NMR (400 MHz, $CDCl_3$): 7.819 (4H, s), 7.4–7.2 (10H, m), 5.529 (2H, s), 4.803 (4H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 167.4, 148.7, 136.3, 132.0, 128.8, 128.6, 128.0, 118.8, 100.1, 61.4, 41.9. HRMS (ESI): m/z calcd for $C_{34}H_{20}Br_2N_2NaO_4$ 702.9667 $[M + Na]^+$, found 702.9612. Compound $\mathbf{13_c}$: ^{1}H NMR (400 MHz, $CDCl_3$): 7.975 (4H, s), 7.53–7.38 (10H, m), 5.636 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 166.7, 149.0, 131.6, 131.1, 129.3, 129.2, 128.4, 126.5, 119.2, 61.5. HRMS (ESI): m/z calcd for $C_{32}H_{16}N_2Br_2NaO_4$ 674.9354 $[M + Na]^+$, found 614.9345.

Dual-cavity baskets $\mathbf{3_{a-c}}$ were prepared following the procedure for obtaining compound **2** in 43, 47, and 27% yield, respectively. Compound $\mathbf{3_a}$. ^{1}H NMR (400 MHz, $CDCl_3$): 7.91 (12H, s), 6.19 (6H, s), 3.57 (12H, t, J = 7.2 Hz), 1.55 (12H, m), 0.85 (18H, t, J = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$): 167.6, 149.1, 135.0, 131.5, 119.0, 50.8, 39.8, 22.0, 11.2. HRMS (ESI): m/z calcd for $C_{78}H_{60}N_6NaO_{12}$ 1295.4161 $[M + Na]^+$, found 1295.4138. Compound $\mathbf{3_b}$. ^{1}H NMR (400 MHz, $CDCl_3$): 7.872 (12H, s), 7.3–7.1 (30H, m), 6.188 (6H, s), 4.741 (12H, s). ^{13}C NMR (100 MHz, $CDCl_3$): 167.2, 149.2, 136.3, 134.8, 131.4, 128.7, 128.5, 127.9, 119.2, 50.7, 46.2. HRMS (ESI): m/z calcd for $C_{102}H_{60}N_6O_{12}Na$ 1584.4200 $[M + Na]^+$, found 1584.4209. Compound $\mathbf{3_c}$. ^{1}H NMR (400 MHz, $CDCl_3$) 8.07 (12H, s), 7.20–7.50 (15H, m), 6.59 (6H, s). ^{13}C NMR (100 MHz, $CDCl_3$): the low solubility of $\mathbf{3_c}$ in a range of solvents prevented us from obtaining a satisfactory ^{13}C NMR spectrum. HRMS (ESI): m/z calcd for $C_{96}H_{48}N_6NaO_{12}$ 1500.3271 $[M + Na]^+$, found 1500.3255.

ASSOCIATED CONTENT

Supporting Information

Copies of $^1H/^{13}C$ NMR spectra and HR ESI-MS data of novel compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported with funds obtained from the National Science Foundation (CHE-1012146 to J.D.B.) and the Department of Defense, Defense Threat Reduction Agency (HDTRA1-11-1-0042 to J.D.B. and C.M.H.). The content of the information does not necessarily reflect the position or the policy of the federal government, and no official endorsement should be inferred. The Ohio Supercomputer Center is gratefully acknowledged for providing generous computational resources.

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